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The final report for AFOSR-86-0081 is attached. A summary of the scientific objectives and accomplishments is reported. Publications resulting from the supported work are listed, as are the names of research personnel, and a list of presentations, seminars, and conferences where the work was discussed. No inventions or patents resulted from the supported work.					
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COMPLETED PROJECT SUMMARY

1. TITLE: Powerful Photogenerated Reducing Agents
2. PRINCIPAL INVESTIGATOR: Professor David Tyler
Department of Chemistry
University of Oregon
Eugene, Oregon 97403
3. INCLUSIVE DATES: April 1, 1986 - March 31, 1988
4. GRANT NUMBER: AFOSR-86-0081
5. COSTS AND FY SOURCE: \$40,000 FY 86; \$40,000 FY 87
6. SENIOR RESEARCH PERSONNEL: Dr. Michael Castellani
7. JUNIOR RESEARCH PERSONNEL: Vivian MacKenzie, Xiong Pan,
Robin Ritter, Cecelia Philbin,
N. D. Silavwe
8. PUBLICATIONS:
 - "Photochemical Generation of Nineteen-Electron Organometallic Complexes and Their Use as Reducing Agents in Micellar Systems." D. R. Tyler, V. MacKenzie and A. S. Goldman, *Proceedings of the Seventh International Conference on the Photochemistry and Photophysics of Coordination Complexes*; H. Yersin and A. Vogler, Eds.; Springer-Verlag: New York, 1987; pp 263-266.
 - "Photochemistry of Organometallic Halide Complexes; Mechanisms for the Formation of Ionic Products." X. Pan, C. E. Philbin, M. P. Castellani and D. R. Tyler, *Inorg. Chem.* 27, 671 (1988).
 - "Reduction of Water-Soluble Substrates in Micellar Solutions Using Photochemically Generated Nineteen-Electron Organometallic Complexes." V. MacKenzie and D. R. Tyler, *J. Chem. Soc., Chem. Commun.* 1783 (1987).
 - "Photochemical Disproportionation Reactions of the $W_2(CO)_{10}^{2-}$ and $Fe_2(CO)_8^{2-}$ Complexes." X. Pan, N. D. Silavwe and D. R. Tyler, *Inorg. Chim. Acta*, 144, 123 (1988).
 - "Structure and Substitution Reactions of Nineteen-Electron Organometallic Complexes." D. R. Tyler, C. E. Philbin and F. Mao, *Proceedings of the NATO Workshop on Paramagnetic Organometallic Species*; St. Maximin, France, Oct. 1987, in press.
 - "Mechanistic Aspects of Organometallic Radical Reactions." D. R. Tyler, *Progress in Inorganic Chemistry*, in press.

"Photochemical Reduction of CO_2 by Nineteen-Electron Complexes." N. D. Silavwe and D. R. Tyler, *J. Am. Chem. Soc.*, submitted for publication.

"Water-Soluble Nineteen-Electron Organometallic Complexes." R. Ritter and D. R. Tyler, manuscript in preparation for *J. Am. Chem. Soc.*

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

An investigation of the reducing abilities of photochemically-generated 19-electron complexes was accomplished. The investigation had four primary objectives: (1) study the capabilities and limitations of the 19-electron complexes as reducing agents; (2) synthesize or produce water-soluble 19-electron complexes; (3) recycle the 19-electron reducing agents so as to make these species catalytic reductants; and (4) use the 19-electron reductants to perform chemically interesting transformations. The first two of these objectives were successfully accomplished, and good progress was made on the last two objectives. The 19-electron complexes are generated by reaction of a photogenerated 17-electron organometallic radical (e.g. $\text{Mn}(\text{CO})_5$, $\text{CpFe}(\text{CO})_2$, $\text{CpMo}(\text{CO})_3$; $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) with a ligand. The dominant reactivity of the 19-electron complexes is electron transfer. Our initial studies established that the oxidation potential of the 19-electron complexes is around 1.5 V vs. SCE, depending on the metal and ligand. Substrates that were reduced in non-aqueous solvents include methylviologen, butylviologen, ferricyanide, $\text{Mn}_2(\text{CO})_{10}$, cobaltocenium, and butyl pyridinium. In order to reduce substrates with reduction potentials more negative than -1.5 V vs. SCE, we developed a technique for photochemically generating the $\text{W}(\text{CO})_5\text{PMe}_2\text{Ph}^-$ complex ($E < -2.0$ V). Using this reductant, we demonstrated the reduction of substrates such as CO_2 and acetophenone. The reduction of water-soluble substrates was accomplished by two methods. The first, but least effective, procedure was to use surfactants and generate the 19-electron reductants in an emulsion. The chief drawback to this method is that the concentrations of the reactants must be low so as to prevent separation of the phases. The low concentrations necessarily prevented practical amounts of substrates from being used. The second method involved the synthesis of the $(\eta^5\text{-C}_5\text{H}_4\text{COO}^-)_2\text{W}_2(\text{CO})_6$ complex. This dimeric precursor to the 19-electron complexes is soluble in water, and consequently the 19-electron complexes can be generated directly in aqueous solution. Using this method, a wide variety of water-soluble substrates were reduced. Attempts to recycle the 19-electron complexes were unsuccessful. A scheme involving homolysis of the metal-halide bond in organometallic halide complexes did not work because photochemical reactions reported in the literature could not be reproduced. An investigation of alternative methods for recycling the 19-electron complexes is continuing in our lab.

Finally, we are also continuing our study of using the 19-electron complexes as initiators of anionic polymerization reactions.

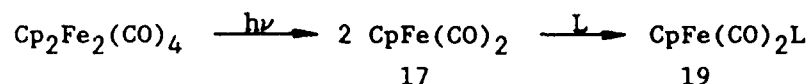
AFOSR Program Manager: Dr. Anthony J. Matuszko

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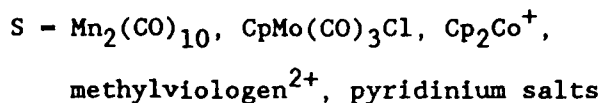


Summary

Nineteen-electron organometallic complexes form by reaction of photochemically generated 17-electron radicals with nucleophiles, e.g.



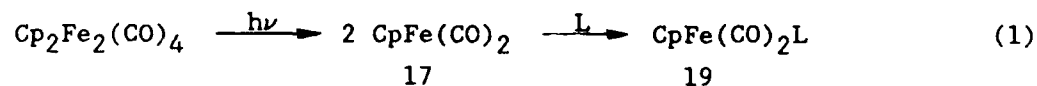
The 19-electron complexes are versatile reducing agents and we demonstrated they can be used to reduce a variety of organic, organometallic, and inorganic complexes:



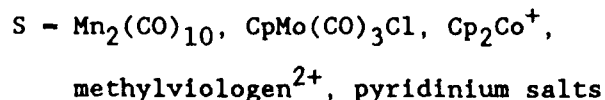
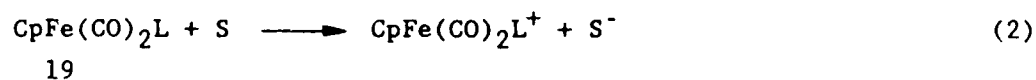
One drawback to the use of the 19-electron complexes as reducing agents is that they cannot be generated in aqueous solution because the dimeric precursor complexes are not water-soluble. To circumvent this problem, we generated the 19-electron complexes in the non-aqueous phase of micellar solutions (emulsions) and reduced substrates in the aqueous phase. A second, more practical method for reducing water-soluble substrates was also devised. The water-soluble $(\text{CpCOO}^-)_2\text{W}_2(\text{CO})_6$ complex was synthesized. Irradiation of this complex and a ligand in aqueous solution produces the water-soluble $(\text{CpCOO}^-)\text{W}(\text{CO})_3\text{L}$ complex; this 19-electron complex can be used to reduce a wide variety of water-soluble substrates, including viologens, cytochrome c, and coordination complexes.

Our investigation of the reactivity of 19-electron organometallic complexes had four primary objectives: (1) study the capabilities and limitations of the 19-electron complexes as reducing agents, (2) develop techniques for generating the 19-electron complexes in aqueous solution, (3) develop techniques for recycling the 19-electron complexes so as to make these species catalytic reductants, and (4) use the 19-electron reductants to perform chemically interesting transformations. The first two of these objectives were successfully accomplished, and excellent progress was made on the last two objectives.

Use of the 19-electron complexes as reducing agents in non-aqueous solution. Nineteen-electron organometallic complexes form by reaction of photochemically generated 17-electron radicals with nucleophiles, e.g.



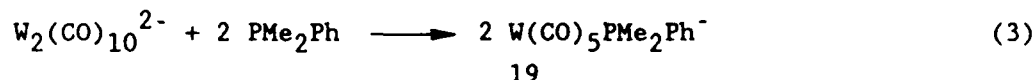
The 19-electron complexes are versatile reducing agents and we demonstrated they can be used to reduce a variety of organic, organometallic, and inorganic complexes:



Attempts to measure the oxidation potentials of the 19-electron complexes (e.g. $\text{CpFe}(\text{CO})_2\text{L}$, $\text{CpMo}(\text{CO})_3\text{L}$) by electrochemical methods were

unsuccessful because the reductions of the corresponding (stable) 18-electron species were irreversible. However, many of the substrates in eq 2 have reduction potentials of at least -1.5 V vs. SCE (e.g. $\text{Mn}_2(\text{CO})_{10}$) so we can put a lower limit of 1.5 V on the oxidation potentials of the 19-electron complexes.

An even more powerful 19-electron reductant is formed when the $\text{W}_2(\text{CO})_{10}^{2-}$ complex is irradiated in the presence of a ligand:



Electrochemical measurements show that the 19-electron $\text{W}(\text{CO})_5\text{PMe}_2\text{Ph}^-$ complex has an oxidation potential of about 2.5 V vs. SCE. Using this reductant, Ned Silavwe in my research group successfully reduced CO_2 (to HCO_2^- , CO, and $\text{C}_2\text{O}_4^{2-}$) and acetophenone (to the radical anion). Details of this work are found in papers #4 and #7 in the section of this report titled "Publications Acknowledging Air Force Support." Two general reviews on the use of 19-electron complexes have also appeared. (See papers #1 and #5 in the "Publications..." section.)

Reduction of water-soluble substrates using 19-electron complexes.

One drawback in the application of the 19-electron complexes is that because they are generated from organometallic precursors they must be used in non-aqueous solvents. Thus, substrates that are soluble only in water cannot be reduced by the 19-electron complexes. This drawback limits the application of these reductants, particularly in problems of biological interest and in solar energy conversion schemes.

Vivian MacKenzie of my research group discovered that the 19-electron complexes can essentially be water-solubilized by generating them in micellar or reverse-micellar solutions. In a typical reaction, $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ and PPh_3 were dissolved in benzene. This solution was added to an aqueous solution containing DDAB or CTAB (DDAB = didodecyl-dimethylammonium bromide; CTAB = hexadecyltrimethylammonium bromide). The combined solutions, consisting of two phases, were then stirred or shaken for about 1 min., after which time the solution was homogeneous with no (visual) evidence of precipitation. The solution was then transferred to the appropriate spectroscopic cell or cuvette and irradiated. The progress of the reaction was monitored spectroscopically. In the case of methylviologen, epr spectra of the reaction solution after irradiation clearly showed the formation of MV^+ . The choice of ligand used to generate the 19-electron complex is not critical. Thus, for example, dppe, PBu_3 , and $\text{P}(\text{OBu})_3$ gave results identical to those obtained above with PPh_3 . Clearly MV^{2+} is reduced in the reaction and it is logical to propose that a 19-electron $\text{CpFe}(\text{CO})_2\text{L}$ complex is the reducing agent. Unfortunately, infrared detection of the $\text{CpFe}(\text{CO})_2\text{L}^+$ cation was impossible in the micellar solution. However, infrared analysis of reactions run in CH_2Cl_2 showed the formation of the cation. In addition, electronic absorption spectroscopic analysis of reactions run in CH_3CN also showed that 2 moles of MV were formed for every mole of $\text{Cp}_2\text{Fe}_2(\text{CO})_4$ consumed, consistent with the stoichiometry in eq 2.

In addition to regular micelles, MV^{2+} can also be reduced in reverse-micelle solutions. The procedure is essentially identical to

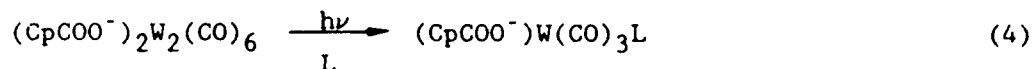
that above except that CTAB is used as the surfactant. MV^+ was again detected by esr spectroscopy.

Other water-soluble/benzene-insoluble products that we have reduced in micellar solution include $Co(NH_3)_6^{3+}$ and $Fe(CN)_6^{3-}$. Reduction of the former species yielded $Co(H_2O)_6^{2+}$ and reduction of the latter species gave Prussian blue. Experimentally, these species were reduced by procedures essentially identical to the one described above for MV^{2+} . $Fe(CN)_6^{3-}$ was reduced in a regular micelle solution while $Co(NH_3)_6^{3+}$ could be reduced in either regular or reverse-micellar solutions.

The pathway involved in the reduction reaction undoubtedly involves the formation of 19-electron species via the pathway in eq 1. However, the details of the electron transfer to the substrate are not clear. In recent work on electron transfer across bilayers it has been shown that the substrate is necessarily bonded to the surfactant by coulombic forces. Clearly, this feature is not a requirement in our systems because, for example, both MV^{2+} and $Co(NH_3)_6^{3+}$ are cationic. Further investigation of the mechanism is continuing in our lab.

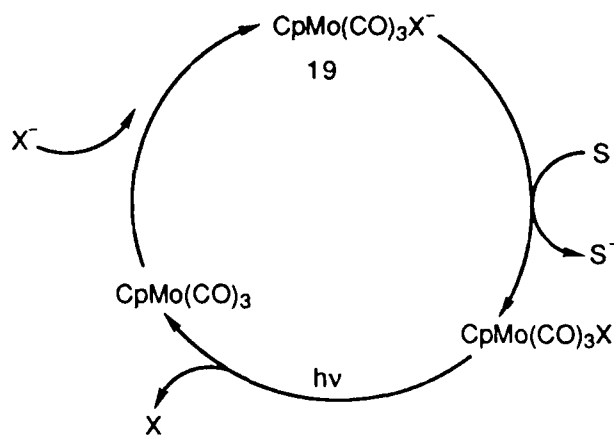
Vivian's work on the micellar systems is published. (See paper #3 in the "Publications..." section of this report.)

A more practical method of generating 19-electron complexes in aqueous solution is to start with a water-soluble dimeric precursor. For this reason, Robin Ritter in my lab synthesized the $(CpCOO^-)_2W_2(CO)_6$ complex ($CpCOO^- = C_5H_4COO^-$). The addition of the carboxylate groups to the Cp rings water-solubilizes the dimer and permits the generation of 19-electron complexes in aqueous solution:



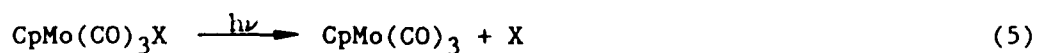
The reduction of water-soluble substrates is now straightforward: the substrate, dimer, and ligand are added to water and irradiated and reduction of the substrate occurs. Robin has reduced a wide variety of substrates using this method. They include various viologens, cytochrome C, $\text{Fe}(\text{phen})_3^{3+}$, TCNQ, and $\text{Fe}(\text{CN})_6^{3-}$. Robin's work is soon to be written up for publication. (See paper #8 in the "Publications..." section of this report.)

Recycling the 19-electron complexes. The third objective of our research is to recycle the 19-electron complexes for use in catalytic schemes. The scheme we worked on is shown below, using $\text{CpMo}(\text{CO})_3\text{L}$ as an example of a 19-electron complex.

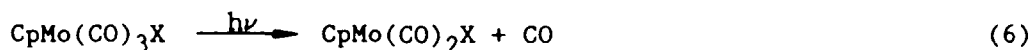


Overall: $\text{X}^- + \text{S} \rightarrow \text{X}\cdot + \text{S}^-$ where X = a halide

Every step of this cycle is a known reaction except for the following:



For that reason, Cecelia Philbin, Xiong Pan, and Mike Castellani in my research group studied the photochemistry of a series of organometallic halide complexes: $\text{CpMo(CO)}_3\text{X}$, $\text{Mn(CO)}_5\text{X}$, and $\text{CpFe(CO)}_2\text{X}$ ($\text{X} = \text{Cl, Br, I}$). Their results established that M-X photolysis does occur but that M-CO bond dissociation also occurs (with a much higher quantum yield), e.g.



Attempts to inhibit the M-CO dissociation were unsuccessful. This work was published. (See paper #2 in the "Publications..." section of this report.)

Use of 19-electron reductants to perform chemically interesting transformations. This objective was the most applied of the four goals listed in the introduction. It was also the lowest of our priorities because we wanted to understand the fundamental principles of 19-electron complex reactivity before undertaking any applied studies. Ned Silavwe briefly worked on this aspect of the project, and he demonstrated that the polymerization of styrene could be initiated using the $\text{W}_2(\text{CO})_{10}^{2-}/\text{PMe}_2\text{Ph}$ system. Presumably, this is an anionic polymerization initiated by the 19-electron $\text{W(CO)}_5(\text{PMe}_2\text{Ph})^-$ complex, but no mechanistic work was done to substantiate this claim.

Publications Acknowledging Air Force Support

1. "Photochemical Generation of Nineteen-Electron Organometallic Complexes and Their Use as Reducing Agents in Micellar Systems." D. R. Tyler, V. MacKenzie and A. S. Goldman, *Proceedings of the Seventh International Conference on the Photochemistry and Photophysics of Coordination Complexes*; H. Yersin and A. Vogler, Eds.; Springer-Verlag: New York, 1987; pp 263-266.
2. "Photochemistry of Organometallic Halide Complexes; Mechanisms for the Formation of Ionic Products." X. Pan, C. E. Philbin, M. P. Castellani and D. R. Tyler, *Inorg. Chem.* **27**, 671 (1988).
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5. "Structure and Substitution Reactions of Nineteen-Electron Organometallic Complexes." D. R. Tyler, C. E. Philbin and F. Mao, *Proceedings of the NATO Workshop on Paramagnetic Organometallic Species*; St. Maximin, France, Oct. 1987, in press.
6. "Mechanistic Aspects of Organometallic Radical Reactions." D. R. Tyler, *Progress in Inorganic Chemistry*, in press.
7. "Photochemical Reduction of CO_2 by Nineteen-Electron Complexes." N. D. Silavwe and D. R. Tyler, *J. Am. Chem. Soc.*, submitted for publication.
8. "Water-Soluble Nineteen-Electron Organometallic Complexes." R. Ritter and D. R. Tyler, manuscript in preparation for *J. Am. Chem. Soc.*

Seminar Presentations Acknowledging Air Force Support

The following presentations dealt with the 19-electron complexes and acknowledged Air Force support.

1. NSF Organometallic Workshop, Austin, Texas; June 1986.
2. 192nd National Meeting American Chemical Society, Anaheim, California; September 1986.

3. Northwest Regional "Snow Symposium," Bend, Oregon; February 1987.
4. Reed College, Portland, Oregon; February 1987.
5. Seventh International Conference on Photochemistry and Photophysics of Coordination Complexes, Klaib, Germany; March 1987.
6. 3M Company, St. Paul, Minnesota; June 1987.
7. NATO Workshop on Paramagnetic Organometallic Species, St. Maximin, France; October 1987.

Personnel

1. Cecelia Philbin, graduate student, Ph.D. expected in August 1988.
2. Vivian MacKenzie, undergraduate, B.S. in June 1987.
3. Robin Ritter, graduate student, Ph.D. expected in about three years.
4. N. D. Silavwe, graduate student, Ph.D. earned in May 1987. Thesis title: "Reduction of CO_2 Using Photogenerated Nineteen-Electron Complexes."
5. Dr. Michael Castellani, postdoctoral associate, now a professor at Marshall College in West Virginia.
6. Xiong Pan, graduate student, terminated from program in January 1987.

AFOSR Program Manager: Dr. Anthony Matuszko